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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Polymer Blends of Cycloolefin Polymers and Polyacetals

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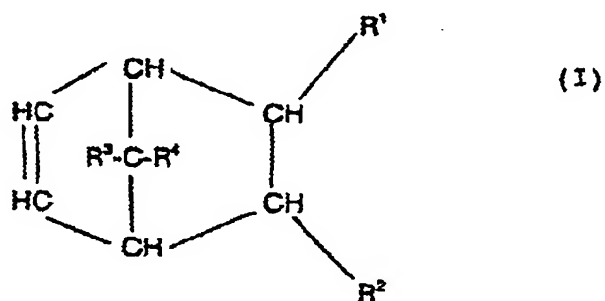
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Abstract of the disclosure

HOE 91/F 275K

Polymer blends of cycloolefin polymers and polyacetals

Polymer blends are prepared from cycloolefin polymers or cycloolefin copolymers and polyacetals by kneading or extruding these together. The cycloolefin polymer preferably comprises structural units which are derived from a monomer of the formula I



Description

Polymer blends of cycloolefin polymers and polyacetals

5 Cycloolefin polymers are a class of polymers which have an outstanding property profile and are distinguished, inter alia, by hydrolytic stability, low absorption of water, resistance to weathering, high heat distortion temperature and transparency.

10 Polyacetals have also been employed for a long time as multi-purpose materials, above all in the engineering sector. Because of their good mechanical properties, such as high rigidity, hardness and strength, as well as the possibility of producing moldings and shaped articles within narrow tolerance limits and the good resistance to
15 many chemicals, they are often suitable as a substitute for metals. In addition to good electrical and dielectric properties, they exhibit favorable slip and wear properties. Because of the good resistance of polyacetals to many organic solvents, they show only slight swelling and
20 a slight drop in their mechanical properties on contact with solvents. In practice, the resistance to automobile gasoline (including that containing methanol), mineral oil and heating oil is of particular importance, this not being guaranteed with cycloolefin polymers.

25 Both polymer classes, cycloolefin polymers and polyacetals, are processed as thermoplastics. Exposure to high temperatures over an extended period leads to decomposition products and oxidation products in the case of the cycloolefin polymers. Shorter intervals of exposure
30 to heat during extrusion and injection molding, i.e. higher output rates by improving the flow properties, would therefore be of advantage. Furthermore, for some uses of polyacetals, for example as matrix materials for

composites, their mechanical properties, for example the modulus of elasticity or the shear modulus, are in need of improvement. In this connection, absorption of water by polyacetals is problematic, since the dimensional stability is not guaranteed at a high ambient humidity. A lower absorption of water would therefore be of advantage.

It is now known that important properties of polymers, such as those mentioned above, can be changed by blending polymers with other polymers. However, the possibility of reliably predicting the properties of a polymer blend from the properties of the individual components is as yet a long way off.

The object of the present invention is therefore to provide polymer blends of cycloolefin polymers and polyacetals having increased flow properties, improved mechanical properties and a lower absorption of water.

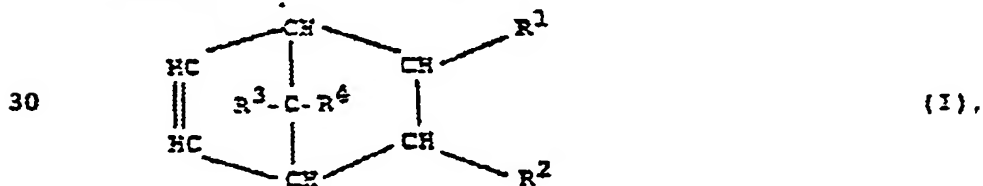
The invention relates to polymer blends comprising at least two components (A) and (B), wherein

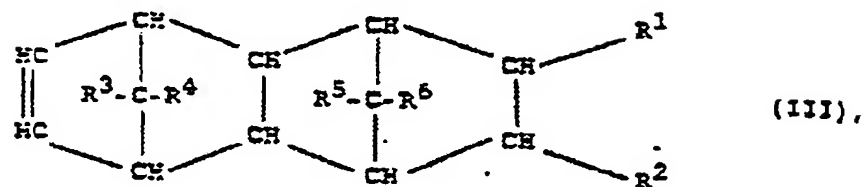
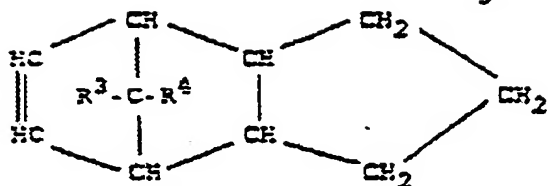
(A) is at least one cycloolefin polymer and

(B) is at least one polyacetal,

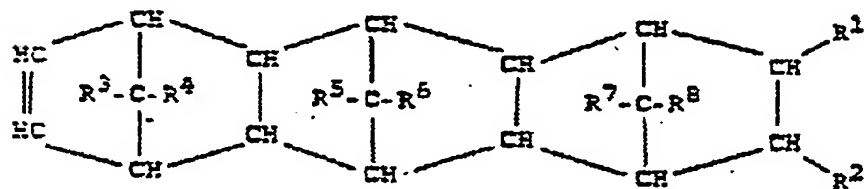
the blends containing (A) in amounts of 1 to 99% by weight and (B) in amounts of 99 to 1% by weight, and the relative amounts of (A) and (B) making up 100% by weight with respect to the total blend.

Cycloolefin polymers (A) which are suitable for the blends according to the invention comprise structural units which are derived from at least one monomer of the formulae I to VI or VII

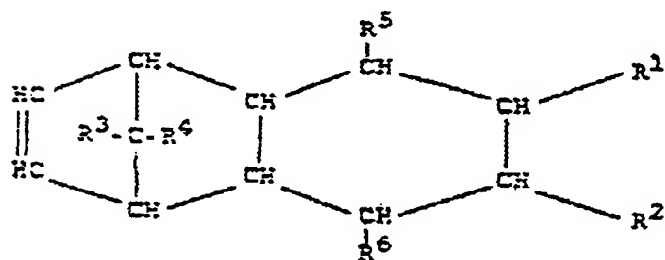




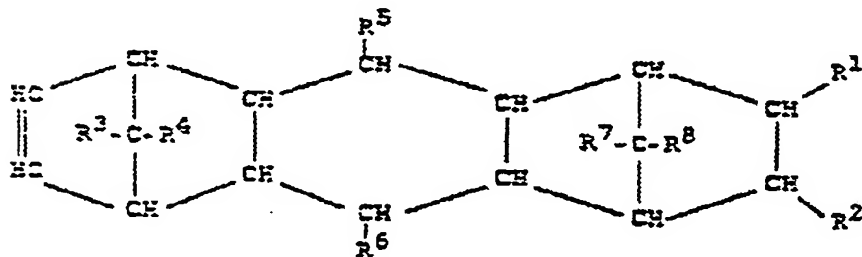
(III),



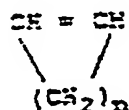
(IV),



(V),



(VI),

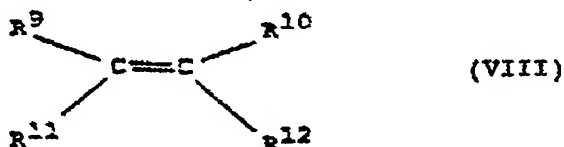


(VII)

in which R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are identical or different and are a hydrogen atom or a C₁-C₈-alkyl radical, it being possible for the same radicals to have different

meanings, in the various formulae and n is an integer from 2 to 10.

The cycloolefin polymers (A) can comprise, in addition to the structural units which are derived from at least one monomer of the formulae I to VII, other structural units which are derived from at least one acyclic 1-olefin of the formula VIII



in which R^9 , R^{10} , R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1 - C_8 -alkyl radical.

Preferred comonomers are ethylene or propylene. Copolymers of polycyclic olefins of the formula I or III and the acyclic olefins of the formula VIII are employed in particular. Particularly preferred cycloolefins are norbornene and tetracyclododecene, which can be substituted by C_1 - C_8 -alkyl, ethylene/norbornene copolymers being of particular importance. Of the monocyclic olefins of the formula VII, cyclopentene, which can be substituted, is preferred. Polycyclic olefins, monocyclic olefins and open-chain olefins are also to be understood as meaning mixtures of two or more olefins of the particular type. This means that cycloolefin homo- and copolymers, such as bi-, ter- and multipolymers, can be employed.

It is known that cycloolefins can be polymerized by means of various catalysts. The polymerization proceeds via ring opening (US-A-3 557 072, US-A-4 178 424) or with opening of the double bond (EP-A-156464, EP-A-283164, E-A-291208, EP-A-291970, DE-A-3922546), depending on the catalyst.

The cycloolefin polymerizations which proceed with opening of the double bond can be catalyzed using more recent catalyst systems (DE-A-39 22 546, EP-A-02 03 799) and also with a conventional Ziegler catalyst system (DD-A-222317, 5 DD-A-239409).

The cycloolefin homo- and copolymers which comprise structural units derived from monomers of the formulae I to VI or VII are preferably prepared with the aid of a homogeneously soluble catalyst comprising a metallocene, 10 the central atom of which is a metal from the group comprising titanium, zirconium, hafnium, vanadium, niobium and tantalum and which forms a sandwich structure with two mono- or polynuclear ligands bridged to one another, and an aluminoxane. The bridged metallocenes are 15 prepared in accordance with a known reaction scheme (cf. J. Organomet. Chem. 288 (1985) 63-67 and EP-A-320762). The aluminoxane, which functions as a cocatalyst, is obtainable by various methods (cf. S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A-302424). The structure 20 and also the polymerization of these cycloolefins are described in detail in DE-A-3 922 546 and in the earlier-priority but not as yet published patent applications DE-A-40 36 264, DE-A-41 06 107 and DE-A-41 07 682. These are cycloolefin copolymers which differ in their chemical 25 uniformity and their polydispersity.

Cycloolefin polymers having a viscosity number greater than 20 cm³/g (measured in decalin at 135°C in a concentration of 0.1 g/100 ml) and a glass transition temperature (T_g) of between 100 and 200°C are preferably 30 employed.

The polymer blends can also comprise cycloolefin polymers which have been polymerized with ring opening in the presence of, for example, catalysts containing tungsten, molybdenum, rhodium or rhenium. The cycloolefin polymers 35 obtained by this process have double bonds which can be

removed by hydrogenation (US-A-3 557 072 and US-A-4 178 424).

The cycloolefin polymers employed for the polymer blends according to the invention can also be modified by grafting with at least one monomer chosen from the group comprising (a) α, β -unsaturated carboxylic acids and their derivatives, (b) styrenes, (c) organic silicone components containing an unsaturated, preferably olefinic, bond and a hydrolyzable group and (d) unsaturated epoxy components. The resulting modified cycloolefin polymers have excellent properties similar to those of the unmodified cycloolefin polymers, and can be employed for the alloys according to the invention either by themselves or together with the unmodified cycloolefin polymers. The modified cycloolefin polymers moreover specifically have a good adhesion to metals and synthetic polymers. The good compatibility with other polymers is to be singled out. It is even possible to prepare, by reactions carried out in solution or in melts, graft copolymers of cycloolefin polymers with polyacetals, which can act as compatibilizers.

Polyacetals (B) which are suitable for the polymer blends according to the invention comprise oxymethylene structural units $[-CH_2-O-]$, preferably in an amount of 80-100% by weight, preferably 90-100% by weight. Such polyacetals (B) are described, for example, in EP-A-0 156 285. Preferred polyacetals (B) are linear, unbranched homo- and copolymers of formaldehyde or its cyclic oligomers, such as trioxane or tetroxane, copolymers being understood as meaning both bi- and multipolymers.

Suitable comonomers are a) cyclic ethers having 3, 4 or 5, preferably 3, ring members, b) cyclic acetals other than tri- or tetroxane and having 5 to 11, preferably 5, 6, 7 or 8, ring members and c) linear polyacetals, in each case in amounts of 0.1 to 20% by weight, preferably

0.5 to 10% by weight. Particularly preferred copolymers contain 99.5 to 95% by weight of oxymethylene structural units and 0.5 to 5% by weight of structural units derived from one of the abovementioned comonomers.

- 5 Homo- and copolymers of formaldehyde or its cyclic oligomers are to be understood as those polymers whose terminal groups have been converted into stable groups after the polymerization.

The polyacetals (B) are prepared by ionic polymerization.

- 10 The homopolymer of polyoxymethylene can be prepared by anionic suspension polymerization of formaldehyde. Esterification with acetic anhydride at about 140°C is then carried out for stabilization of the unstable hemi-acetal end groups. For the preparation of copolymers,
15 trioxane is first prepared from an approximately 60% strength aqueous formalin solution in the presence of sulfuric acid. The monomeric trioxane, which has been carefully purified by distillation, can then be polymerized cationically in bulk in the presence of a few
20 percent by weight of ethylene oxide or 1,3-dioxepane (butanediol formal) at about 70°C. The unstable hemi-acetal end groups of the resulting copolymer are finally converted into stable alcoholic end groups. An overview of the essential process steps and evaluation of the
25 numerous patents and publications is given in Process Economic Program (G.E. Haddeland, Report No. 69, Acetal Resins, Stanford Research Institute, Menlo Park, California 1971).

- The inherent viscosity of the polyacetals (B) is in
30 general 0.3 to 2.0 dl/g, preferably 0.5 to 1.5 dl/g (measured in butyrolactone, stabilized with 2% by weight of diphenylamine, at 140°C in a concentration of 0.5 g/100 ml) and the melt volume indices (MVI), determined in accordance with DIN 53735-B, are in general 0.02 to
35 70 cm³/10 minutes, measured at 190°C under a load of

2.16 kg. The crystalline melting point (T_m) is in general 140-180°C, preferably 150-170°C.

The polyacetals employed for the blends according to the invention can also be modified by grafting with suitable functional compounds comprising diisocyanates, as coupling agents, and corresponding functional masking agents. The term "functional masking agents" is understood as meaning monomeric or polymeric compounds having one or two functional groups per chain, for example hydroxyl, carboxyl or amino groups, which can undergo addition reactions with diisocyanates. Suitable functional masking agents are, for example, mono- and difunctional polyalkylene oxides, polyesters, polyamides, polyolefins, polydienes and polysiloxanes. Polyacetals modified by grafting are described in EP-A-0 397 493.

These block or graft copolymers can be employed as engineering resins per se or as compatibilizers with other polymers.

The blends according to the invention preferably comprise 5 to 95% by weight, particularly preferably 10 to 90% by weight, of the cycloolefin polymers (A), and conversely 95 to 5% by weight or 90 to 10% by weight of the polyacetals (B), the relative amounts of components A and B making up 100% by weight with respect to the total blend. The blends according to the invention can contain one or more cycloolefin polymers and one or more polyacetals, as well as modified cycloolefin polymers, modified polyacetals and/or block and/or graft copolymers of these.

Blends which comprise modified cycloolefin polymers, in addition to unmodified cycloolefin polymers and polyacetals, exhibit, for example, a finer dispersion, ie. smaller particle sizes. Extremely fine dispersion occurs in blends in which the total content of cycloolefin polymers is modified. These blends also have surprisingly

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good mechanical properties.

The blends according to the invention are prepared and processed by standard methods known for thermoplastics, for example by kneading, extrusion or injection molding.

- 5 The blends according to the invention can comprise additives, for example heat stabilizers, UV stabilizers, antistatics, flameproofing agents, plasticizers, slip agents and lubricants, pigments, dyestuffs, optical brighteners, processing auxiliaries and inorganic and
10 organic fillers, ie. in particular also reinforcing additives, such as glass fibers, carbon fibers or high modulus fibers.

- The blends can advantageously be employed as a matrix material for composite materials. Moreover, they are
15 suitable for the production of shaped articles, for example in the form of sheets, fibers, films and tubes, by the injection molding or extrusion process.

The following polymers were prepared by standard methods:

Cycloolefin copolymer A1 [COC A1]

- 20 A) Preparation of diphenylmethylen-(9-fluorenyl)-cyclopentadienyl-zirconium dichloride (metallocene L)

All the following working operations were carried out in an inert gas atmosphere using absolute solvents (Schlenk technique).

- 25 12.3 cm³ (30.7 mmol) of a 2.5 molar solution of n-butyl-lithium in hexane were slowly added to a solution of 5.1 g (30.7 mmol) of fluorene in 60 cm³ of tetrahydrofuran at room temperature. After 40 minutes, 7.07 g (30.7 mmol) of diphenylfulvene were added to the orange solution, and
30 the mixture was stirred overnight. 60 cm³ of water were

added to the dark red solution, whereupon the solution became yellow in color, and the solution was extracted by shaking with diethyl ether. The ether phase was dried over MgSO_4 and concentrated, and the residue was left to
5 crystallize at -35°C . 5.1 g (42% by weight) of 1,1-cyclopentadienyl-(9-fluorenyl)-diphenylmethane were obtained as a beige powder.

2.0 g (5.0 mmol) of the compound were dissolved in 20 cm^3 of tetrahydrofuran, and 6.4 cm^3 (10 mmol) of a 1.6 molar
10 solution of butyllithium in hexane were added at 0°C . After the mixture had been stirred at room temperature for 15 minutes, the solvent was removed under reduced pressure, and the red residue was dried under an oil pump vacuum and washed several times with hexane. After the
15 red powder had been dried under an oil pump vacuum, it was added to a suspension of 1.16 g (5.00 mmol) of ZrCl_4 in 20 ml CH_2Cl_2 at -78°C . After the mixture had been warmed up slowly, it was stirred at room temperature for a further 2 hours. The pink-colored suspension was filtered over a G3 frit.
20 The pink residue was washed with 20 cm^3 of CH_2Cl_2 , dried under an oil pump vacuum and extracted with 120 cm^3 of toluene. After the solvent had been removed under reduced pressure and the residue had been dried under an oil pump vacuum, 0.55 g of the zirconium complex was obtained in
25 the form of a pink crystalline powder.

The orange-red filtrate of the reaction mixture was concentrated and the residue was left to crystallize at -35°C . A further 0.45 g of the complex crystallizes from CH_2Cl_2 .

30 Total yield 1.0 g (36% by weight). Correct elemental analyses. The mass spectrum showed $M^+ = 556$. $^1\text{H-NMR}$ spectrum (100 MHz, CDCl_3): 6.90-8.25 (m, 16, Flu-H, Ph-H), 6.40 (m, 2, Ph-H), 6.37 (t, 2, Cp-H), 5.80 (t, 2, Cp-H).

B) Preparation of COC A1 (ethylene/norbornene copolymer)

- A clean and dry 75 dm³ polymerization reactor with a stirrer was flushed with nitrogen and then with ethylene, and 30 l of an 85% strength by weight toluene solution of norbornene (Nb) were introduced. The reactor was then brought to a temperature of 70°C, while stirring, and ethylene was passed in until a pressure of 3.5 bar was established.
- 580 cm³ of a toluene solution of methylaluminoxane (10.1% by weight of methylaluminoxane having a molecular weight of 1300 g/mol according to cryoscopic determination) were then metered into the reactor, and the mixture was stirred at 70°C for 15 minutes, the ethylene pressure being kept at 3.5 bar by topping up. In parallel with this, 500 mg of metallocene L were dissolved in 500 cm³ of a toluene solution of methylaluminoxane (for the concentration and quality, see above) and were preactivated by being left to stand for 15 minutes. The solution of the complex (catalyst solution) was then metered into the reactor. Hydrogen may be used to regulate the molecular weight. Polymerization was then carried out at 70°C for 140 minutes, while stirring (750 revolutions/minute), the pressure in the reactor being kept at 3.5 bar by topping up with ethylene. The contents of the reactor were then drained rapidly into a stirred vessel, into which 200 cm³ of isopropanol (as a stopper) had been introduced. The mixture was precipitated in acetone and stirred for 10 minutes, and the suspended polymeric solid was filtered off.
- A mixture of two parts of 3 N hydrochloric acid and one part of ethanol was then added to the polymer which had been filtered off, and the mixture was stirred for 2 hours. The polymer was filtered off again, washed neutral with water and dried at 80°C under 0.2 bar for 15 hours.
- An amount of product of 4500 g was obtained.

Cycloolefin copolymers A2 [COC A2] and A3 [COC A3]

A) Preparation of rac-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride (metallocene A)

5 All the following working operations were carried out in an inert gas atmosphere using absolute solvents (Schlenk technique).

80 cm³ (0.20 mol) of a 2.5 molar solution of n-butyl-lithium in hexane were added to a solution of 30 g (0.23 mol) of indene (industrial grade, 91%), which had
10 been filtered over aluminum oxide, in 200 cm³ of diethyl ether, while cooling with ice. The mixture was stirred at room temperature for a further 15 minutes, and the orange-colored solution was passed via a cannula into a solution of 13.0 g (0.10 mol) of dimethyldichlorosilane
15 (99% pure) in 30 cm³ of diethyl ether in the course of 2 hours. The orange-colored suspension was stirred overnight, and extracted three times by shaking with 100-150 cm³ of water. The yellow organic phase was dried twice over sodium sulfate and evaporated in a rotary evaporator.
20 The orange oil which remained was kept at 40°C under an oil pump vacuum for 4 to 5 hours and freed from excess indene, a white precipitate being obtained. A total of 20.4 g (71% by weight) of the compound (CH₃)₂Si(Ind)₂ could be isolated as a white to beige powder by addition
25 of 40 cm³ of methanol and crystallization at -35°C. Melting point 79-81°C (2 diastereomers).

15.5 cm³ (38.7 mmol) of a 2.5 molar solution of butyl-lithium in hexane were slowly added to a solution of 5.6 g (19.4 mmol) of (CH₃)₂Si(Ind)₂ in 40 cm³ of tetrahydrofuran at room temperature. One hour after the
30 addition had ended, the deep red solution was added dropwise to a suspension of 7.3 g (19.4 mmol) of ZrCl₄·2-tetrahydrofuran in 60 cm³ of tetrahydrofuran in the course of 4-6 hours. After the mixture had been stirred for

2 hours, the orange precipitate was filtered off with suction over a glass frit and recrystallized from CH_2Cl_2 . 1.0 g (11% by weight) of $\text{rac}-(\text{CH}_3)_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ was obtained in the form of orange crystals, which gradually
5 decompose above 200°C . Correct elemental analyses. The mass spectrum showed $M^+ = 448$. ^1H -NMR spectrum (CDCl_3): 7.04-7.60 (m, 8, aromatic H), 6.90 (dd, 2, β -Ind H), 6.08 (d, 2, α -Ind H), 1.12 (s, 6, SiCH_3).

10 B) Preparation of COC A2 and COC A3 (ethylene/norbornene copolymers)

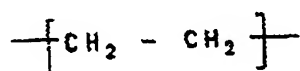
COC A2 and COC A3 were prepared analogously to COC A1, some of the conditions summarized in Table 1 being changed.

Table 1

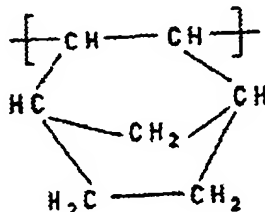
Cyclo- olefin copolymer	85% strength by weight norbornene [l]	Tempera- ture [°C]	H ₂ metering [l/h]	Pressure [bar]	Metallocene Type Amount [mg]	Catalyst solution [ml]	Poly- merization time [minutes]	Amount of product [g]
A2	31	70	0.5	12	A 520	750	180	4400
A3	32	70	1.0	25	A 470	500	220	4600

Metallocene A: rac-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride

The physical parameters of the three cycloolefin copolymers which comprise structural units of the formula F1 and F2



F1



F2

5 can be seen from Table 2.

Table 2

10	Cyclo- olefin copoly- mer	Incorporation* of		VN	<Mw> · 10 ⁻⁵ [g/mol]	<Mn> · 10 ⁻⁴ [g/mol]	<Mw> [g/mol]	Tg Ø [°C]
		Ethyl- ene [mol %]	Nor- bornene [mol %]					
15	A1	49	51	166	2.25	10.2	2.2	178
	A2	55	45	91	0.92	4.5	2.0	143
	A3	59	41	83	0.82	3.5	2.3	114

20 * determined by ¹³C nuclear magnetic resonance spectroscopy

VN: viscosity number determined in accordance with DIN 53728

25 <Mw>, <Mn>: gel permeation chromatography: 150-C ALC
Millipore Waters Chromatograph
Column set: 4 Shodex columns AT-80 M/S
Solvent: o-dichlorobenzene at 135°C

Flow rate: 0.5 ml/minute, concentration
0.1 g/dl

RI detector, calibration: polyethylene (901
PE)

- 5 Ø Heating up and cooling down rate: 20°/minute

Other characteristics of the cycloolefin copolymers A1,
A2 and A3 can be seen from the examples.

Cycloolefin graft copolymers A3-P1* [COC A3-P1] and A3-P2+
[COC A3-P2+] and A3-P3 [COC A3-P3]

- 10 1. Preparation of COC A3 (A3-P1* and A3-P2+), grafted with
maleic anhydride

20 g (108.1 g/l) of COC A3 were dissolved in 150 ml of
toluene (thiophene-free, absolute) in a clean and dry
500 ml two-necked flask connected to an inert gas supply
15 (consisting of an oil pump for generating a high vacuum,
and an argon feed for aeration). When the copolymer had
dissolved completely, 8 g (438.6 mmol/l) of maleic
anhydride (MA, 99% pure) were added and dissolved, before
2 g (27.1 mmol/l) of dilauroyl peroxide (dissolved in
20 35 ml of toluene (thiophene-free, absolute)) were added.
The contents of the flask were degassed completely at
-196°C (four freezing/degassing cycles). Argon was then
applied and the reaction solution was introduced into an
oil bath preheated at a controlled temperature of 80°C.

- 25 Free radical grafting of MA onto COC A3 was ended after
5½ hours by precipitation in 2 l of acetone. For working
up, ie. purification of the polymer, this was reprecipi-
tated in acetone four times, 16.3 g of MA-grafted cyclo-
olefin polymer A3 (A3-P1*) being obtained after drying at
30 130°C (72 hours/oil pump vacuum).

A3-P2+ was prepared analogously, 2.8 g (38.0 mmol/l) of
dilauroyl peroxide being employed. Yield: 15.9 g

FT-IR [cm^{-1}]: 1865 ss / 1790 ss (C=O, anhydride)
VN [cm^3/g]: in accordance with DIN 53728
A3-P1* : 85.7; A3-P2+ : 84.2

5 2. Preparation of COC A3 (A3-P3), grafted with maleic anhydride

A clean and dry 2 l two-necked flask was filled with argon. 70 g (90.0 g/l) of COC A3, dissolved in 700 ml of toluene (absolute, were introduced in an argon counter-current. 19.0 g (250.3 mmol/l) of maleic anhydride (MA, 99% pure) were then added in countercurrent to the inert gas and dissolved, before 6.68 g (21.8 mmol/l) of dilauroyl peroxide (dissolved in 70 ml of toluene (absolute)) were likewise added in a countercurrent of argon. The reaction solution was introduced into an oil bath, preheated at a controlled temperature of 80°C, and stirred vigorously with a precision glass stirrer. Free radical grafting of MA onto COC A3 was ended after 5½ hours by precipitation in 5 l of acetone. For working up, ie. purification of the polymer, the latter was reprecipitated four times in acetone, 66 mg of MA-grafted cycloolefin copolymer A3 (A3-P3) being obtained after drying at 130°C (72 hours/oil pump vacuum).

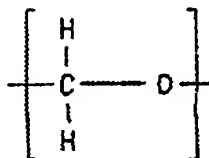
25 FT-IR [cm^{-1}]: 1865 ss / 1790 ss (C=O, anhydride)
VN [cm^3/g]: in accordance with DIN 53728
A3-P3 : 86.7

The absolute contents of MA in the graft copolymer were determined by means of potentiometric titration.

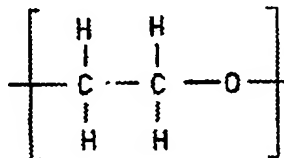
Table 3

5	Sample	MA content [% by weight]	Average number of MA/ polymer chain A3
	A3-P1*	1.07	4
	A3-P2+	1.95	7
10	A3-P3	0.64	2

Polyacetal B having structural units of the formula F3 and F4



F 3



F 4

15 in which the content of oxymethylene structural units is 98% by weight and the content of oxyethylene structural units is 2% by weight.

Such a polyacetal B is commercially available. It is marketed, for example, as *Hostaform C 2521 (* = registered
20 trademark) by Hoechst AG, Frankfurt am Main.

The polymers described above were first dried (130°C, 24 hours, vacuum) and then kneaded or extruded under a protective gas (Ar) in a measuring kneader (HAAKE (Karlsruhe), Rheocord System 40/Rheomix 600) or measuring
25 extruder (HAAKE (Karlsruhe), Rheocord System 90/Rheomax TW 100). The resulting ground or granulated blends were dried (130°C, 24 hours, vacuum) and then pressed (vacuum press: Polystat 200 S, Schwabenthan (Berlin)) to give

5 sheets (120 x 1 mm). The ground or granulated blends were introduced into the press, which had been preheated to 230°C (blends with A1 and A2) or 190°C (blends with A3 and graft copolymers A3-P1^{*} and A3-P2⁺ or blends with graft copolymer A3-P3), a vacuum was applied and the blends were melted in the course of 10 minutes. The material was pressed together under a pressure of 150 bar at the above temperature, this pressure was maintained for 5 minutes and the sheets were then cooled to room temperature in the course of 10 minutes. The resulting melt-pressed sheets were investigated in respect of their physical properties.

The following apparatus was used for this:

15 A differential scanning calorimeter (DSC-7) from Perkin-Elmer (Überlingen) for measurement of, for example, glass stages, melting points and heats of fusion.

A torsion pendulum machine from Brabender (Duisburg) for measurement of the shear modulus, damping and linear expansion.

20 A tensile stress-elongation test machine (type: Instron 4302) from Instron (Offenbach).

25 A melt index tester MPS-D from Goettfert (Buchen) for measurement of flow properties in accordance with DIN 53735-MVI-B (plunger load/temperature variable; barrel: internal diameter 9.55 (\pm 0.01) mm, length at least 115 mm, discharge nozzle 2.095 (\pm 0.005) mm, melting time 5 or 10 minutes).

The water content was determined in accordance with ASTM D 4019-81.

Example 1:

The cycloolefin copolymer (A1) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The following tables shows the thermal properties determined on the blends.

	COC A1 [% by weight]	POM B [% by weight]	Cooling		2nd Heating		
			Tm [°C]	ΔHm [J/g]	Tm [°C]	ΔHm [J/g]	Tg [°C]
			POM B		POM B		COC
10	100	0	--	--	--	--	178
15	70	30	141	43.8	168	37.7	179
	50	50	140	88.7	168	75.9	*
	30	70	141	125.5	167	114.7	*
20	0	100	142	168.4	168	171.2	-

Heating up and cooling down rate: 20°/minute

* not measurable (sensitivity of the apparatus too low)

25 Example 2:

The cycloolefin copolymer (A1) and the polyacetal (B) were mixed together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader, and the mixture was then ground. After intensive drying, the ground products were used to measure the flow properties.

5	COC A1 [% by weight]	POM B [% by weight]	MVI 21.6 kg/230°C [cm ³ /10 minutes] Melting time 5 minutes
	100	0	23.5
	70	30	110.6
10	50	50	305.7
	30	70	391.1
15	0	100	74.4

Example 3:

The cycloolefin copolymer (A2) and the polyacetal (B) were extruded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the twin-screw extruder, and the extrudate was granulated. After intensive drying, the granules were used to measure the flow properties.

5	COC A2 [% by weight]	POM B [% by weight]	MVI 21.6 kg/220°C [cm ³ /10 minutes] Melting time 5 minutes
	100	0	14.2
	70	30	198.9
10	50	50	445.4
	30	70	not measurable (> 450)
15	0	100	62.0

Example 4:

The cycloolefin copolymer (A2) and the polyacetal (B) were extruded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the twin-screw extruder, and the extrudate was granulated. After intensive drying, the granules were then pressed to give pressed sheets. The following table shows the mechanical data determined on the blends in the tensile stress/elongation experiment.

COC A2 [% by weight]	POM B [% by weight]	Modulus of elasticity [GPa]	Yield stress [MPa]
100	0	3.2	62
70	30	3.0	59
50	50	2.8	58
30	70	2.9	58
0	100	2.8	58

Example 5:

The cycloolefin copolymer (A3) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The following table shows the thermal properties determined on the blends.

	COC A3 [% by weight]	POM B [% by weight]	Cooling		2nd Heating		
			Tm POM B [°C]	ΔHm [J/g]	Tm POM B [°C]	ΔHm COC [J/g]	Tg [°C]
5	100	0	--	--	--	--	114
10	70	30	142	x	168	x	114
	50	50	141	x	167	x	*
	30	70	142	x	168	x	*
15	0	100	142	168.4	168	171.2	-

Heating up and cooling down rate: 20°C/minute

x Separation not possible (melting point, glass stage)

* not measurable (sensitivity of the apparatus too low)

20 Example 6:

The cycloolefin copolymer (A3) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The ground products were dried intensively and, after storage at 23°C and 85% relative humidity for at least 240 hours, the absorption of water was determined.

	COC A3 [% by weight]	POM B [% by weight]	Water content [% by weight]
5	100	0	0.01
	70	30	0.10
	50	50	0.16
10	30	70	0.29
	0	100	0.41

15 Example 7:

The cycloolefin copolymer (A3) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The ground products were dried intensively and pressed to give pressed sheets. The following table shows the mechanical data of the blends during the torsion pendulum test.

COC A3 [% by weight]	POM B [% by weight]	Shear modulus G' (torsion pendulum) [N/mm ² mm] Temperature [°C]											
		-141	-61	-31	20	40	56	70	85	101	111	120	140
100	0	1541	1083	1050	983	950	914	870	821	715	505	--	--
70	30	1626	1077	996	890	834	781	733	682	592	415	--	--
50	50	2105	1264	1085	912	833	747	671	609	526	379	114	29
30	70	2736	1550	1248	1007	889	753	638	549	446	330	151	67
0	100	3787	1947	1388	1022	866	695	576	477	378	310	249	148

Example 8:

The cycloolefin copolymer (A3) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were used to measure the flow properties.

10	COC A3 [% by weight]	POM B [% by weight]	MVI 21.6 kg/190°C [cm ³ /10 minutes] Melting time 5 minutes
	100	0	15.3
15	70	30	89.4
	50	50	159.0
	30	70	189.3
20	0	100	38.2

Example 9:

The cycloolefin copolymer (A3), the graft copolymer A3-Pa⁺ and A3-P2⁺ and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The following table shows the thermal properties determined on the blends.

	COC A3 [% by weight]	COC A3-P1*/2+ [% by weight]	POM B [% by weight]	Cooling		2nd Heating		
				Tm [°C]	ΔHm [J/g] POM B	Tm [°C]	ΔHm [J/g] POM B	Tg [°C] COC
5	100	0	0	--	--	--	--	114
10	70	0	30	142	x	167	x	114
	56	14*	30	142	x	167	x	113
	18	12+	70	143	x	167	x	V
15	30	0	70	142	x	167	x	V
	0	0	100	142	168.4	168	171.2	--

Heating up and cooling down rate: 20°C/minute

20 x Separation not possible (melting point, glass stage)

* not measurable (sensitivity of the apparatus too low)

Example 10:

25 The cycloolefin copolymer (A3), the graft copolymer (A3-P1* and A3-Ps+) (compatibilizer) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were used to measure the flow properties.

5	COC A3 [% by weight]	COC A3-P1 [*] /-P2+ [% by weight]	POM B [% by weight]	MVI 21.6 kg/190°C [cm ³ /10 minutes] Melting time: 5 / 10 minutes
	100	0	0	15.3 / 15.5
10	70	0	30	89.4 / 96.7
	56	14 [*]	30	64.3 / 71.2
	18	12 ⁺	70	171.6 / 181.6
15	30	0	70	189.3 / 188.9
	0	0	100	38.2 / 37.2

20 Example 11:

25 The cycloolefin copolymer (A3), the graft copolymer (A3-P1^{*} and A3-P2+) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were pressed to give pressed sheets. The following table shows the mechanical data determined on the blends with/without the compatibilizer (A3-P1^{*} and A3-P2+) in the torsion pendulum test.

2077411

COC A3 [% by weight]	COC A3-P1* A3-P2+ [% by weight]	POM B [% by weight]	Shear modulus G' (torsion pendulum) [N/mm ² mm] Temperature [°C] -141 -61 -31 20 40 56 70 85 101 111 120 140
100	0	0	1541 1083 1050 983 950 914 870 821 715 505 -- --
70	0	30	1626 1077 996 890 834 781 733 682 592 415 -- --
56	14*	30	1858 1194 1075 942 875 807 753 698 585 398 -- --
18	12+	70	2716 1599 1275 1013 906 776 689 595 475 334 168 70
30	0	70	2736 1550 1248 1007 889 753 638 549 446 330 151 67
0	0	100	3787 1947 1388 1022 866 695 576 477 378 310 249 148

Example 12:

The cycloolefin copolymer (A3), the graft copolymer (A3-P1⁺ and A3-P2⁺) and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were pressed to give pressed sheets. The following table shows the mechanical data determined on the blends with/without a compatibilizer (A3-P1⁺ and A3-P2⁺) in the tensile stress/elongation experiment.

COC A3 [% by weight]	COC A3-P1 ⁺ A3-P2 ⁺ [% by weight]	PDM B [% by weight]	Modulus of elasticity [GPa]	Yield stress [GPa]	Elongation at break [%]
100	0	0	3.1	60	4.9
70	0	30	2.9	57	5.0
56	14 ⁺	30	3.0	57	3.6
18	12 ⁺	70	2.8	60	10.2
30	0	70	2.8	56	5.4
0	0	100	2.8	58	35.0

Example 13:

The graft copolymer A3-P3 and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. The following table shows the thermal

properties determined on the blends.

5	COC A3-P3 [% by weight]	POM B [% by weight]	Cooling		2nd Heating		
			T _m [°C]	ΔH _m [J/g]	T _m [°C]	ΔH _m [J/g]	T _g [°C]
			POM B		POM B	COC	
	100	0	--	--	--	--	113
10	70	30	83/114 ⁺	x	162	33	112
	30	70	143	x	168	x	V
15	0	100	142	168.4	168	171.2	-

Heating up and cooling down rate: 20°C/minute

x Separation not possible (melting point, glass stage)

V not measurable (sensitivity of the apparatus too low)

+ several minima (2nd main minimum)

20 Example 14:

The graft copolymer A3-P3 and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground
25 products were used to measure the flow properties.

5	COC A3-P3 [% by weight]	POM B [% by weight]	MVI 21.6 kg/190°C [cm ³ /10 minutes] Melting time 5 / 10 minutes
	100	0	14.6 14.8
10	70	30	7.8 7.9*
	30	70	9.3 7.0
15	0	100	38.2 37.2

* foam-like material

Example 15:

The cycloolefin copolymer A3 or the graft copolymer A3-P3 and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were pressed to give pressed sheets. The following table shows the mechanical data determined on the blends in the torsion pendulum test.

COC A3 [% by weight]	COC A3-P3 [% by weight]	POM B [% by weight]	Shear modulus G' (torsion pendulum) [N/mm ² mm]										
			Temperature [°C]										
			-141	-61	-31	20	40	56	70	85	101	111	120 140
100	0	0	1541	1083	1050	983	950	914	870	821	715	505	-- --
0	100	0	1442	1053	1020	946	906	867	835	798	666	372	-- --
70	-	30	1626	1077	996	890	834	781	733	682	592	415	-- --
-	70	30	1834	1216	1119	990	919	851	797	740	619	416	-- --
-	30	70	2768	1586	1291	1028	899	764	680	586	464	323	162 69
30	-	70	2736	1550	1248	1007	889	753	638	549	446	330	151 67
0	0	100	3787	1947	1388	1022	866	695	576	477	378	310	249 148

Example 16:

The graft copolymer A3-P3 and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were pressed to give pressed sheets. The following table shows the mechanical data determined on the blends in the tensile stress/elongation experiment.

10	COC A3-P3 [% by weight]	POM B [% by weight]	Elasticity modulus [GPa]	Yield stress [MPa]	Elongation at break [%]
	100	0	3.1	61	5.0
15	70	30	2.9	56	7.9
	30	70	2.9	58	17.8
20	0	100	2.8	58	35.0

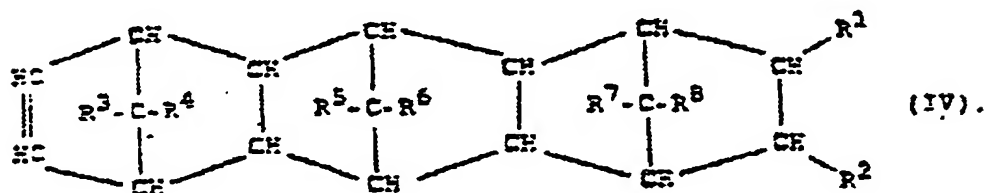
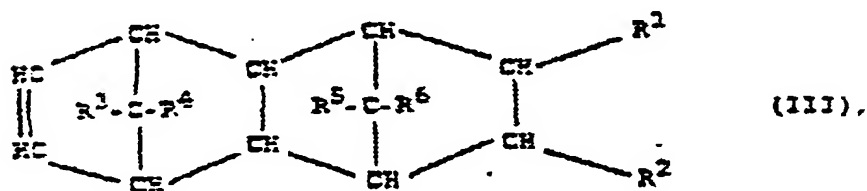
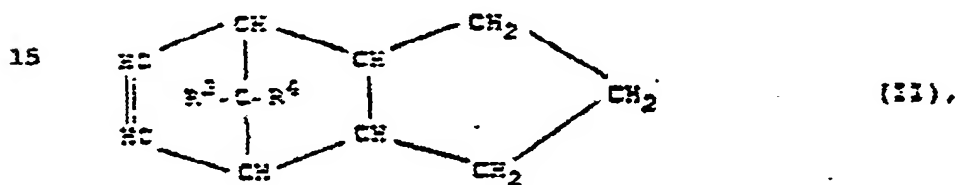
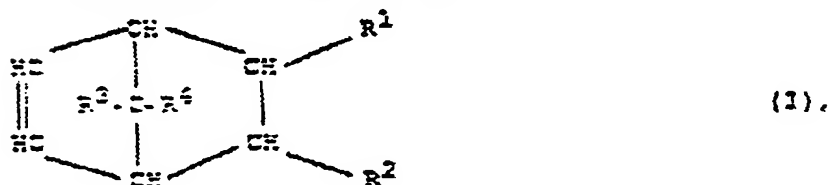
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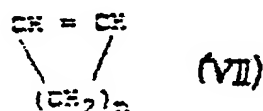
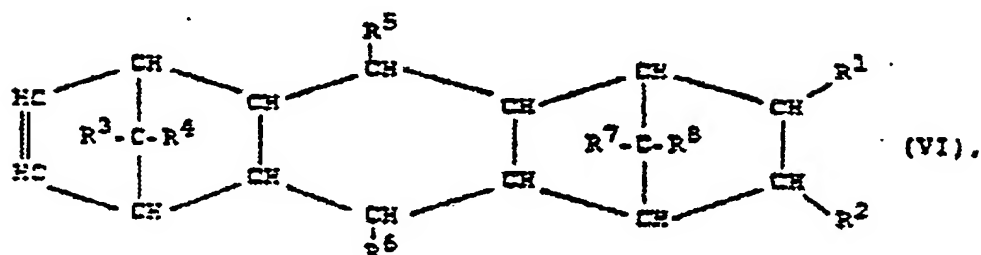
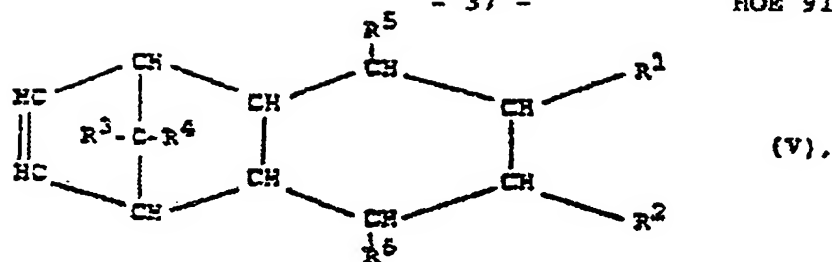
The graft copolymer A3-P3 and the polyacetal (B) were kneaded together, after intensive drying, in various weight ratios under an argon atmosphere by means of the measuring kneader. After intensive drying, the ground products were pressed to give pressed sheets. The following table shows the mechanical data determined on the blends in the tensile stress/elongation experiment.

10	COC A3-P3 [% by weight]	POM B [% by weight]	Elasticity modulus [GPa]	Yield stress [MPa]	Elongation at break [%]
	100	0	3.1	61	5.0
15	70	30	2.9	56	7.9
	30	70	2.9	58	17.8
20	0	100	2.8	58	35.0

Patent Claims:

1. A polymer blend comprising at least two components (A) and (B), wherein (A) is at least one cycloolefin polymer and (B) is at least one polyacetal, the blend containing (A) in amounts of 1 to 99% by weight and (B) in amounts of 99 to 1% by weight, and the relative amounts of (A) and (B) making up 100% by weight with respect to the total blend.
- 5
- 10 2. A polymer blend as claimed in claim 1, wherein the cycloolefin polymer (A) comprises structural units which are derived from at least one monomer of the formulae I to VI or VII





in which R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 are identical or different and are a hydrogen atom or a C_1 - C_8 -alkyl radical, it being possible for the same radicals to have different meanings in the various formulae, and n is an integer from 2 to 10.

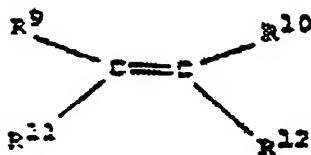
5

3. A polymer blend as claimed in claim 2, wherein the cycloolefin polymer (A) is modified by grafting with at least one monomer chosen from the group comprising (a) α, β -unsaturated carboxylic acids and their derivatives, (b) styrenes, (c) organic silicone components containing an unsaturated bond and a hydrolyzable group, and (d) unsaturated epoxy components.

10

4. A polymer blend as claimed in one of claims 2 or 3, wherein the cycloolefin copolymer (A) comprises, in addition to the structural units which are derived from at least one monomer of the formulae I to VII, other structural units which are derived from at least one acyclic 1-olefin of the formula VIII

15

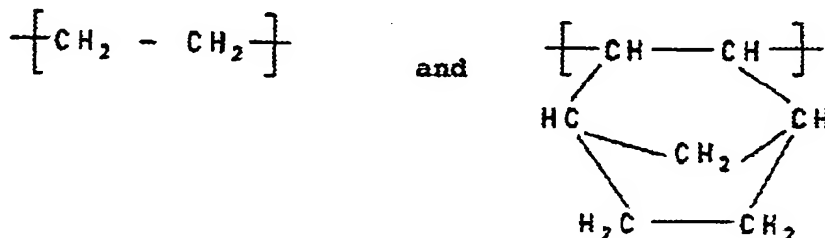


(VIII)

in which R^9 , R^{10} , R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1 - C_8 -alkyl radical.

5. A polymer blend as claimed in claim 4, wherein the cycloolefin polymer (A) is a copolymer of polycyclic olefins of the formula I or III and at least one acyclic olefin of the formula VIII.
6. A polymer blend as claimed in claim 5, wherein the cycloolefin polymer (A) is a copolymer of norbornene and ethylene.
7. A polymer blend as claimed in claim 1, wherein the polyacetal (B) comprises oxymethylene structural units $[-CH_2-O-]$ in an amount of 80 - 100% by weight.
8. A polymer blend as claimed in claim 7, wherein the polyacetal (B) comprises, in addition to the oxymethylene structural units, structural units derived from comonomers selected from the group comprising
 - a) cyclic ethers having 3, 4 or 5 ring members, b)
 - cyclic acetals other than tri- or tetraoxane and
 - having 5 to 11 ring members and c) linear polyacetals.
9. A polymer blend as claimed in claim 8, wherein the amount of oxymethylene structural units is 99.5 to 95% by weight and the amount of structural units derived from the comonomers mentioned is 0.5 to 5% by weight, with the proviso that the various amounts make up 100% by weight.

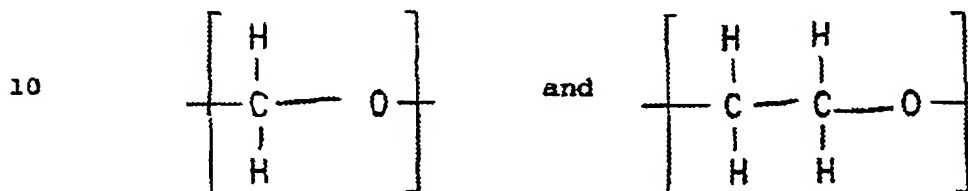
10. A polymer blend as claimed in claim 9, wherein the polyacetal (B) comprises oxymethylene structural units and oxyethylene structural units.
11. A polymer blend as claimed in claim 1, wherein the cycloolefin polymer (A) is a copolymer having structural units of the formulae



F 1

F 2

and the polyacetal (B) is a copolymer having structural units of the formulae



F 3

F 4

12. A polymer blend as claimed in one of claims 1 or 11, which additionally comprises a cycloolefin polymer (A) modified by grafting with at least one monomer chosen from the group comprising (a) α, β -unsaturated carboxylic acids and their derivatives, (b) styrenes, (c) organic silicone components containing an unsaturated bond and a hydrolyzable group, and (d) unsaturated epoxy components.
13. A polymer blend as claimed in claim 11, which additionally comprises a cycloolefin copolymer (A)

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